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Effective charge on silicon atom in the metal silicides Mg_2Si and CaSi

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The effective charges of Si in both magnesium (Mg_2Si) and calcium silicides (CaSi and Ca_2Si) have been investigated by measuring high-resolution Si $K\alpha$ x-ray fluorescence spectra. CaSi showed small but positive chemical shifts (+0.03 eV), while the chemical shift of Mg_2Si was negative (−0.14 eV), as expected from their electronegativity (Ca: 1.00; Mg: 1.31; Si: 1.90). The similarity of the chemical shift for the Fe silicides and the calculations for the free single Si atom suggested that the effective charge of Si for CaSi was positive. From the observations the effective charges on Si in CaSi and Mg_2Si were estimated to be +0.1 and −0.3 electrons. The discrete variation Hartree-Fock-Slater calculations for Mg_2Si and CaSi also showed opposite chemical shifts and effective charges: −0.09 eV and −0.35 electrons for Mg_2Si and +0.09 eV and +0.26 electrons for CaSi , respectively. The composition of the nearest-neighbor atoms of Si, which are Si in CaSi and Mg in Mg_2Si , cause the opposite effective charges between the two silicides.

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I. INTRODUCTION

The effective charge is useful to understand the chemical bond between silicon and neighboring metal atoms in metal silicides. Here the silicides are, in a narrow sense, sometimes defined as M_3Si ($M=\text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu} \cdots$) but we consider various kinds of metal-silicon binary compounds as silicides in the present paper. A practical parameter to determine the effective charge of binary compounds is the electronegativity proposed by Mulliken¹ or Pauling.^{2,3} The electronegativity of Si is 1.90, and the metal electronegativities are 1.66 for Cr, 1.55 for Mn, 1.83 for Fe, 1.88 for Co, 1.91 for Ni, 1.90 for Cu, 1.31 for Mg, and 1.00 for Ca.^{4,5} The electronegativity defined by Pauling is “the power of an atom in a molecule to attract electrons to itself.” Therefore if we apply the electronegativity to a H_2S molecule or a SiF_6^{2-} cluster, the effective charge is clearly defined. However, for solids, it is sometimes difficult to apply the electronegativity to define the effective charge of each atom. The electronegativity is at least a good parameter to determine whether each atom is either positively charged or not, depending on the neighbor atoms. Based on the difference of electronegativities, the effective charge on Si in most of the silicides except for Ni are negative values; metal is charged plus, and silicon is charged minus. For nickel silicides, J.-H. Xu and Y.-N. Xu⁶ calculated the charge transfer of Ni_3Si and NiSi_2 using the self-consistent linear muffin-tin orbital (LMTO) method. Their results showed that 0.1 electrons were transferred from two Si atoms to a Ni atom for NiSi_2 , and 0.03 were transferred for Ni_3Si . The total number of electrons within the Ni sphere increased, but the Ni d electrons decreased. The overall effective charge on the Si atom in nickel silicides is positive, which is in good agreement with that estimated from the electronegativity of nickel; the electronegativity of Ni is slightly larger than that of silicon as defined by Mulliken and Pauling. However, recently some of the present authors⁷

measured the chemical shift of Si $K\alpha_{1,2}$ x-ray lines for iron silicides and found that silicon was positively charged, despite that the electronegativity of silicon is larger than that of iron. The characteristic x-ray emission lines $K\alpha_{1,2}$ are emitted from a core-hole transition from $1s^{-1}$ to $2p^{-1}$. The chemical shift is strongly correlated to the effective charge of the x-ray emitting atom.^{8–10} Leonhardt and Meisel⁸ calculated the chemical shifts of $K\alpha$ for elements of the third period according to the free-ion model and presented the dependence on the effective charges. The chemical shift was positive when the atom was charged positive, whereas the shift was negative for the negatively charged atom. Petrovitch *et al.*¹¹ also pointed out that a smaller effective number of electrons in the valence band shifts the inner-shell electrons to higher binding energies, which cause a higher energy for the $K\alpha$ emission line. The effective charges increased the $K\alpha_{1,2}$ line ($K-L_{3,2}$) shifted to higher energy, which meant that the deep shift in the K shell was larger than that of the L shell. The electronegativity of the neighbor atoms changed the effective charges on the Si atoms and caused the chemical shift. A comparison with the chemical shift and the effective charge enables us to identify the chemical state of the atoms in unknown compounds quantitatively.¹²

Thus, the positive energy shifts of the Si atoms in Fe silicides seemed somewhat strange, because the electronegativity of Si was larger than that of Fe. To elucidate chemical bonding in metal silicides, we investigated the chemical shifts and the effective charges of Si in Ca and Mg silicides, where the electronegativity of Ca and Mg was much smaller than that of Si. We measured the Si $K\alpha$ x-ray fluorescence spectra of Mg_2Si , CaSi , and CaSi_2 and also calculated the chemical shifts and the effective charges of these compounds. We will present the plus charge of the Si atoms in calcium silicides, while the Si atoms in Mg_2Si had a minus effective charge.

II. EXPERIMENTAL SECTION

The Si $K\alpha$ x-ray fluorescence spectra were measured on a high-resolution double-crystal-vacuum x-ray fluorescence spectrometer (Rigaku, Japan), with two InSb(111) ($2d = 0.74806$ nm) as analyzing crystals. A W-anode tube was operated at 35 kV and 20 mA as an excitation source. Si $K\alpha$ x-rays were monochromatized by using two InSb(111) crystals and were detected with a FPC flow proportional counter. The details of the instrumental setup have been described elsewhere.¹³ The measured Mg_2Si sample was a slug. The powder specimens (CaSi and $CaSi_2$) were pressed into briquettes. The Si used as a reference was a commercial wafer as received. The fluorescence spectra were recorded in a stepwise mode with a step of 0.01° in 2θ , i.e., 0.05 eV at 1740 eV. The average counting rates at peak maximum were about 15, 40, and 65 counts for Mg_2Si , CaSi, and $CaSi_2$, respectively. That of the pure Si reference was 250 counts. The dwell times were 40 s for Mg_2Si and CaSi, 20 s for $CaSi_2$, and 10 s for Si, respectively. Before and after each sample measurement, we measured the spectra of pure Si to check the reproducibility and calibrated the energy shift (± 0.01 eV) of the monochromators due to the change of the temperature. The spectra were plotted in an energy scale.

III. RESULTS AND DISCUSSION

The Si $K\alpha$ spectra of Si, Mg_2Si , CaSi, and $CaSi_2$ are shown in Fig. 1 after normalization with respect to peak maximum. The measured spectra were numerically smoothed 10 times by the least-squares method of Savitzky and Golay^{14–16} (second order, seven points). The chemical shifts in Table I were defined as the energy change of Si $K\alpha$ doublets. Here, we use the center energy of the full width at $\frac{9}{10}$ of the $K\alpha$ peak maxima.¹⁷ The Si $K\alpha$ spectra of Mg_2Si shifted to lower energy (-0.14 eV), while the chemical shift of the Si $K\alpha$ spectra in CaSi was small, but positive ($+0.03$ eV). The chemical shift of $CaSi_2$ was also positive ($+0.01$ eV), but almost 0. With pure Si as a reference, the $K\alpha_1$ peak of pure Si was located at 1740 eV. As mentioned above, the error for the determination of the peak position was 0.01 eV, so the error of the chemical shift was estimated to be 0.02 eV. We also attempted the curve fitting by using the smoothed Si $K\alpha$ spectrum of pure silicon, and the obtained chemical shifts agreed within the error. In general, the direction of the chemical shifts is related to the effective charge of the concerning atom. The chemical shifts of Si $K\alpha$ and the effective charges of the Si atoms showed a good correlation when the neighbor atom of Si went from B to F.⁷ This leads to the result that the Si atoms of CaSi and $CaSi_2$ would be positively charged, while effective charge of Si in Mg_2Si would be negative. On the contrary, the electronegativity of these elements increases in the order of $Ca < Mg < Si$ (Ca: 1.00; Mg: 1.31; Si: 1.90; defined by Pauling^{2,5}). This suggests that the Si atoms in these silicides are all negatively charged. The theoretical calculation with the ADF (Amsterdam Density Functional) program (Scientific Computing & Modeling NV, The Netherlands) for the “ $Mg_2Si(Mg-Si\ 0.27\text{ nm})$ molecular” gave $+0.185$ elec-

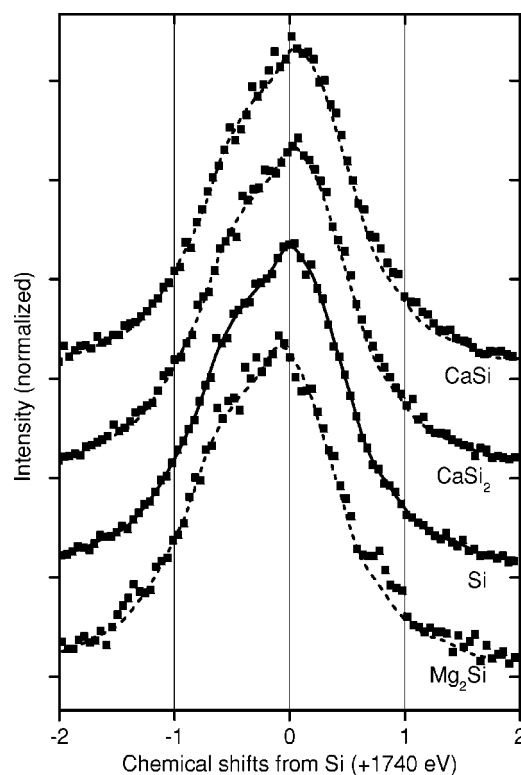


FIG. 1. The Si $K\alpha$ x-ray fluorescence spectra of Mg and Ca silicides. Dot: the raw experimental data. Solid line: The Si $K\alpha$ x-ray spectrum after the Savitzky-Golay smoothing, the parameters of which are given in the text. The broken lines represent the curve-fitting spectra by using the smoothed Si $K\alpha$ spectrum of pure Si.

trons and -0.370 electrons for the effective charges on the Mg and Si atoms, respectively. A similar calculation for the CaSi (Ca—Si 0.32 nm) also resulted in -0.372 electrons for the charge on the Si atom.

To elucidate this contradiction, we calculated the effective charges and the chemical shift of Si $K\alpha$ for a free single Si atom by using the discrete variational (DV) Hartree-Fock-Slater ($X\alpha$) method.^{18–20} As shown in Table II and Fig. 2, the chemical shift was negative when Si had a negative charge, while positive charges induced positive shifts. From this point of view, it could be concluded that the Si in CaSi is positively charged whereas the effective charge of Si in Mg_2Si is negative. On the contrary, Kawai and co-workers^{17–21} pointed out that chemical shifts of the $K\alpha$ lines for 3d transition metals showed the opposite peak shifts, whether the ionization of electrons occurred from the 3d orbital or the 4s orbital. For Ti^* , the $3d^2 4s^1$ state induced a positive chemical shift, while the $3d^1 4s^2$ ionization showed a negative shift, even if the effective charge of Ti is the same. For CaSi, if back bonding from the Ca atoms to the Si atom occurred, the Si 3d orbital would be occupied. As shown in Table II, the discrete variation Hartree-Fock-Slater (DV $X\alpha$) calculation for a free Si atom with a negative charge (-1 electron) also indicated a positive chemical shift ($+0.31$ eV) for Si^- when one electron occupied the 3d state. Thus, two possible causes for the positive chemical shift of CaSi were considerable: (i) a positive charge on Si and (ii) a negative charge on Si with a Si 3d contribution to Ca—Si bonding.

TABLE I. The chemical shifts for the Si $K\alpha$ lines of the Mg and Ca silicides and the effective charges on the Si atoms.

| Samples | Measured chemical shifts for Si $K\alpha$ lines (eV) | Effective charges on Si (electrons per Si atom) | Calculated chemical shifts (eV) | Calculated effective charges (electrons per Si) |
|--------------------|--|---|---------------------------------|---|
| Mg ₂ Si | -0.14 ± 0.02 | -0.3 | -0.09 | -0.35 |
| CaSi | $+0.03 \pm 0.02$ | +0.1 | +0.09 | +0.26 |
| CaSi ₂ | $+0.01 \pm 0.02$ | | | |

However, the energy of the $3d$ orbital of Si is usually sufficiently high in the unoccupied continuum level. Therefore, the chemical bonds of the transition metal silicides have been generally described in terms of the hybridization between the metal d and the silicon p state.^{22,23} The bonding in the calcium silicides has been also explained as a general hybridization between the Ca s - p - d and Si s - p states.²⁴ The theoretical partial density of state with the Si- s , Si- p , and Si- d electronic states for β -FeSi₂,^{36,37} in which the positive chemical shift of Si $L_{2,3}$ was reported,³⁸ indicated that the ratio of the number of Si s , p , and d states was about 3:5:1. Thus, we can neglect the role of the Si $3d$ orbital in Ca—Si chemical bonding. Si in CaSi should be considered as a positively charged atom.

Bisi *et al.*²⁴ calculated chemical bond and electronic states in calcium silicides (Ca₂Si, CaSi, and CaSi₂), compared with photoemission. One of their results was that the chemical bonding between Si and Ca was not simple, mixing with covalency and ionicity, and that the strength of the bonding increased with the Si concentration, increasing the number of filled Ca $3d$ states. Jia *et al.*²⁵ also measured Ca L and Si L fluorescence spectra of CaSi and CaSi₂ and concluded that the bonding between Si and Ca was as covalent as that of pure Si. Liu *et al.*⁷ measured the Si K spectra of both FeSi and FeSi₂ and concluded that Si had a positive charge, whereas the relative electronegativities of Fe and Si were 1.83 and 1.90, respectively.

In contrast, the x-ray photon spectroscopy (XPS) results for calcium silicides,^{26,27,29–31} and in particular CaSi, are ambiguous because of the surface sensitivity of this method. These results have been obtained mainly for the silicide films on Si surfaces with a Ca deposition. At the initial stage of the film's growth, the Si $2p$ photoelectron spectra showed a larger negative chemical shift (1.1–1.45 eV), while a smaller

negative chemical shift (0.3–0.4 eV) was observed after the CaSi₂ films formed.^{26,27} Schöpke *et al.*²⁷ concluded that a larger chemical shift arose from the formation of the Ca-rich silicides, such as Ca₂Si and CaSi. The local structure of the Si atoms in CaSi, however, resembles that of CaSi₂ rather than Ca₂Si, where the nearest-neighbor atoms of Si are Ca atoms, because the nearest-neighbor atom of Si in CaSi₂ is not Ca but Si.^{24,28} The Si LLV Auger line-shape measurements and the theoretical density of states corresponding to the Si atoms in calcium silicides²⁹ suggested that the electronic state of the Si in CaSi seemed to be an intermediate state between those of Ca₂Si and CaSi₂. Therefore, a larger negative charge on Si atoms in CaSi could not be expected. It should be noted that the positive Si $2p$ chemical shift of the component, which was assigned to Si in the second layer below the Ca atom in the one-dimensional (1D) Ca chain, have been observed in the Ca/Si(111)-(2×1) and (3×1) surfaces.^{30,31}

Thus, it is concluded that the effective charge of the Si atoms in CaSi is positive. The difference between the chemical shifts of FeSi and FeSi₂ was 0.02 eV,⁷ which was comparable with that between CaSi and CaSi₂ obtained in this work (0.02 eV). As mentioned above, the Fe atoms in both silicides had positive effective charges. This similarity of the Fe—Si bisystems supports the conclusion that the small positive charge exists in the Si atoms of CaSi. Thus it is concluded that the positively charged Si caused the small positive chemical shift of the Si $K\alpha$ spectra for CaSi.

While calcium silicides can be formed as Ca₂Si, CaSi, and CaSi₂, Mg₂Si is the only possible stoichiometry for magnesium silicides.³² Every Si atom is surrounded by eight nearest-neighbor Mg atoms. Thus, the electron transfer from Mg to Si may easily occur. Si $2p$ XPS results for Mg₂Si on Si(100) (Ref. 33) and Si(111) (Ref. 34) also showed negative

TABLE II. The DVX α calculations of the chemical shift of the free single Si atom.

| Si valence state | $3s^23p^1$ | $3s^23p^2$ | $3s^23p^3$ | $3s^23p^23d^1$ |
|--------------------------|------------|------------|------------|----------------|
| Total charge | +1 | 0 | -1 | -1 |
| (electrons per Si atoms) | | | | |
| Si $2p$ (eV) | -99.68 | -85.88 | -73.00 | -74.24 |
| Si $1s$ (eV) | -1780.33 | -1765.92 | -1752.57 | -1754.59 |
| Si $2p$ –Si $1s$ (eV) | 1680.65 | 1680.04 | 1679.57 | 1680.35 |
| Chemical shifts (eV) | 0.61 | 0.00 | -0.47 | 0.31 |

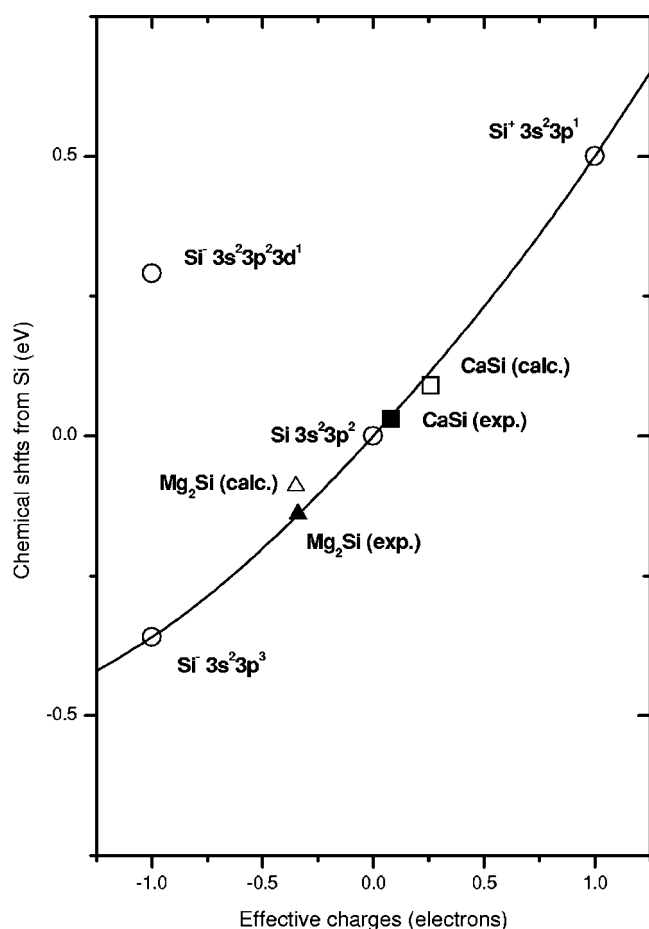


FIG. 2. The correlation between the effective charges on Si and the chemical shifts in the Si $K\alpha$ lines. Open circle: DVX α calculations for the free single Si atom. The open triangle and square represent calculations for Mg₂Si (Mg₈Si cluster) and CaSi (Ca₈Si cluster), respectively. The closed triangle and square indicate measured ones for Mg₂Si and CaSi, respectively.

chemical shifts. The results presented in this paper for Mg₂Si agreed with this XPS study and the ordinary understanding for the charge state of Si. As shown in Fig. 2 and Table I, the effective charges of Si in both silicides were estimated as -0.3 electrons for Mg₂Si and $+0.1$ electrons for CaSi, respectively, according to the Si free-atom calculations. The nearest-neighbor atoms in both silicides induced this difference in effective charges between CaSi and Mg₂Si, although the electronegativities of Ca and Mg are smaller than that of Si.

Finally, we calculated the effective charges on Si atoms in Mg₂Si and CaSi by using the DVX α method. For the Mg₂Si (the anti-CaF₂ type)³⁵ we used a cubic Mg₈Si model cluster, and the bond length of Si—Mg was 0.275 nm. However, the

CaSi crystalizes in a CrB-type structure (TII antistructure),²⁸ where the nearest atoms to Si are the two nearest-neighbor Si atoms with a bond length of 0.247 nm and seven Ca atoms at the second nearest-neighbor site with bond lengths of 0.311 to 0.323 nm. At first we neglected the nearest-neighbor Si atoms for comparison with the Mg silicides. A Ca₈Si model cluster with the Si—Ca bond length of 0.320 nm was also applied. Effective charges on the Si atoms were -0.35 electrons for Mg₂Si and $+0.26$ electrons for CaSi, which caused chemical shifts of -0.09 and $+0.09$ eV, respectively (Table I). Compared with the measured chemical shifts shown in Fig. 2, the calculated effective charged in CaSi was overestimated, and the Ca—Si bonding was more covalent than the calculated one. This difference might have been expected, because the nearest-neighbor Si atoms and the Si—Si covalent bonding were neglected. However, the trend of chemical bonding in these silicides was reproduced. Although the Mg₂Si was more ionic than the CaSi, chemical shifts and effective charges of both silicides were smaller than those of the other Si compounds in Ref. 7. This suggests that the chemical bonding in the Ca and Mg silicides has a more covalent character.

IV. CONCLUSION

The chemical bonding of Mg₂Si, CaSi, and Ca₂Si has been investigated by the interpreting Si $K\alpha$ x-ray fluorescence spectra obtained from a high-resolution double-crystal x-ray fluorescence spectrometer. Although the electronegativity of Mg (1.31) and Ca (1.00) were smaller than that of Si (1.90), chemical bonding in both the Mg and Ca silicides shows different behaviors. The negative chemical shift of Si $K\alpha$ in Mg₂Si showed that the effective charge of Si was negative, as expected from electronegativity. On the contrary, a small but positive chemical shift in the CaSi spectrum suggested that the Si was charged positively, as observed in Fe silicides (FeSi and FeSi₂), although the electronegativity of Ca is smaller than that of Mg and Si. The Si atoms located at the nearest neighbor of Si in CaSi produced positively charged Si and covalency in Ca—Si chemical bonding. DVX α calculations also reproduced this trend of chemical bonding in both silicides. The present study showed agreement with the conventional understanding for the Si charges in Mg silicide, but was completely opposite for Ca silicides, as reported for Fe silicides.

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